

## Magnetism in small vanadium clusters

Feng Liu, S. N. Khanna, and P. Jena

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

(Received 17 October 1990)

Using the self-consistent-field molecular-orbital theory and the density-functional approximation, we show that vanadium could become magnetic if its size and dimension were constrained. This is illustrated for vanadium forming clusters with body-centered-cubic (bcc) geometry as well as for linear chains. The magnetic moment of the bcc clusters is found to vanish abruptly as the size increases, while the clusters always retain their moment in the linear-chain configurations. The moments are also found to be finite for large interatomic spacings irrespective of the cluster topology, and tend to vanish when the interatomic distances are reduced. The results are explained by using a simple Stoner criterion.

It is well known that all transition-metal atoms carry a finite magnetic moment due to the Hund's-rule coupling in their unfilled  $d$  shells. However, only a few of those atoms are able to retain these moments in the bulk environment, and that too at a much reduced level.<sup>1</sup> These general results are illustrated in Fig. 1. What is not well understood is why and how an atom loses its moment as it goes from free space into a solid.<sup>2,3</sup> It is hoped that a fundamental understanding of this striking behavior may lead us to design materials of controlled size and dimension that may be magnetic while their bulk counterparts are not.

Studies of the magnetism of materials with changing interatomic spacing, dimension, and size have been of interest for a long time. For example, Akoh and Tasaki<sup>4</sup> reported observations of magnetism in small particles of vanadium ranging from 100 to 1000 Å in size. Conklin *et al.*<sup>5</sup> showed that vanadium undergoes a transition from a paramagnetic to a ferromagnetic configuration as the lattice parameter is increased. Similar conclusions were also reached by Moruzzi *et al.*<sup>6</sup> who carried out a self-consistent band-structure calculation of  $3d$  elements as a

function of lattice spacing. Salahub and Messmer,<sup>7</sup> using the scattered wave- $X_\alpha$  technique studied the magnetism of a  $V_{15}$  cluster and found that it became magnetic when the interatomic spacing was increased. Pelligatti *et al.*<sup>8</sup> also showed that even simple metals like K could exhibit magnetic behavior by increasing the lattice constant. However, none of these authors have studied the evolution of the magnetism of vanadium clusters as a function of cluster size. While the above studies clearly reveal that clusters and bulk metals tend to favor magnetism as the interatomic separation is increased, it is not at all clear what role does the size of a cluster play on their magnetism. For example, is a small cluster more likely to be magnetic while the larger cluster is not assuming that both the clusters have the same interatomic spacing?

In this article we illustrate this possibility by confining our theoretical studies to vanadium only. We have sought answers to the following questions. (1) Can a cluster of vanadium atoms exhibit magnetic behavior? (2) If so, what is the critical size of the cluster for which the system would become paramagnetic as in the crystalline state? (3) Does a cluster cease to be magnetic gradually or precipitously as its size increases? (4) How does the magnetic behavior of vanadium clusters change as we change their topology, dimensionality, and interatomic spacing?

We have investigated these issues by calculating self-consistently the electronic structure, density of states, and total energies of vanadium clusters consisting of up to 51 atoms confined to bcc geometry as well as linear chains for varying interatomic distance. The results are based upon the local density approximations to the density-functional theory and the discrete variational method.<sup>9</sup> We have found that a 9-atom cluster of  $V$  atoms confined to the bcc geometry and having bulk lattice constant is antiferromagnetically coupled with the central atom carrying less than half the moment of the surface atoms. However, these moments go abruptly to zero for a 15-atom cluster and cannot recover their magnetism as clusters begin to grow. On the other hand,  $V$  atoms confined to linear chains are ferromagnetically coupled and retain their moment for any length of chain.

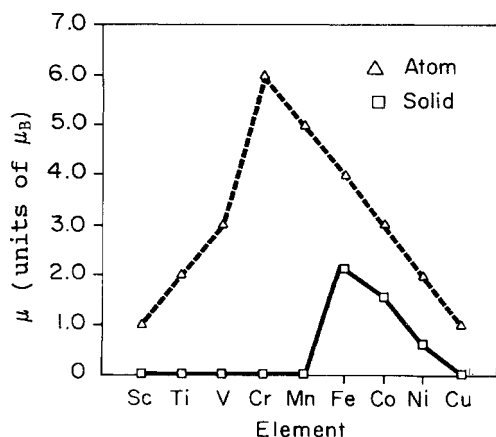


FIG. 1. Spin magnetic moment of the atoms and the bulk magnetic moments for the  $3d$  transition elements.

We have also observed that  $V$  atoms can retain their moments if their interatomic distances are artificially stretched<sup>6</sup> and can lose their moments in the reverse procedure. These results can be easily understood using the simple Stoner criteria.<sup>10</sup> In the following we present details of our calculational method and results.

We have used the self-consistent-field linear combination of atomic orbitals molecular-orbital (SCF-LCAO-MO) method. Consider a system of  $N$  particles described by a one-electron Hamiltonian  $H$  in atomic units

$$H = -\frac{1}{2}\nabla^2 + \int \frac{\rho(\mathbf{r}')d^3r'}{|\mathbf{r}-\mathbf{r}'|} + \sum_j \frac{Z_j}{|\mathbf{r}-\mathbf{R}_j|} + V_{xc}^\sigma(\mathbf{r}). \quad (1)$$

Here  $j$  is the atomic-site index. The second and the third terms represent, respectively, the electronic and nuclear contribution to the electrostatic energy. The last term is the exchange correlation contribution to the potential for spin  $\sigma$  and is approximated by the von Barth-Hedin approximation<sup>11</sup> to the local-spin density (LSD) functional. The wave function  $\psi_i$  for the system is expressed as a linear combination of atomic orbitals  $\phi_i$  localized at the site  $i$ .  $\sigma$  denotes the spin-orbital index.

$$\psi_i = \sum_j C_j \phi_j. \quad (2)$$

$C_i$  are variational coefficients to be determined from a solution of the Rayleigh-Ritz equation

$$(\underline{H} - E\underline{S})\underline{C} = 0, \quad (3)$$

where  $\underline{H}$  and  $\underline{S}$  are the Hamiltonian and overlap matrices and  $E$  is the eigenvalue. This equation was solved by using the discrete variational method<sup>9</sup> (DVM), where the Hamiltonian and overlap matrix elements are evaluated as weighted sums over a set of points  $r_k$  with weight function  $\omega(r_k)$ , namely,

$$H_{ij} = \sum_k \omega(r_k) \phi_i^*(r_k) H \phi_j(r_k), \quad (4)$$

$$S_{ij} = \sum_k \omega(r_k) \phi_i^*(r_k) \phi_j(r_k).$$

In short, the DVM scheme involves use of numerical atomic basis in the construction of molecular orbitals. In the present work, we have used  $3s^2$ ,  $3p^6$ ,  $3d^3$ ,  $4s^{1.99}$ , and  $4p^{0.01}$  configurations for the atomic basis functions to generate the molecular valence orbitals. The rest of the core orbitals were frozen. The secular equation was then solved self-consistently using matrix elements obtained via three-dimensional numerical integrations performed

on a grid of random points by the Diophantine method. About 3 000 sampling points around each atom was used. These points were found to be sufficient for convergence of the electronic spectrum within 0.01 eV and the binding energy within 0.1 eV. The details of the method are well documented in literature,<sup>12</sup> and are not repeated here.

To satisfy ourselves that the choice of the basis functions and numerical procedure are reliable, we have calculated the bond length, binding energy, and ground-state configuration of  $V$  dimer for which both experiments and previous calculations are available. We find  $V_2$  to have a triplet ground state with a bond length of 3.3 a.u. and binding energy of 3.50 eV. This is in very good agreement with previous theoretical values<sup>13</sup> of 3.3 a.u. and 3.84 eV. These authors<sup>13</sup> also found the ground state to be spin triplet. The experimental bond length<sup>14</sup> is 3.34 a.u. and the ground state is spin triplet.

The magnetic moment is obtained by integrating the density of states for each spin up to the Fermi energy and then taking the difference. The spin density of states around each atom can be obtained by summing over Lorentzian lines of width  $\gamma$  centered at the molecular-orbital energies,

$$D_n^\sigma(E) = \sum_j f_{nj} \frac{\pi/\gamma}{(E - E_j)^2 + \gamma^2}, \quad (5)$$

where  $f_{nj}$  are atomic populations taken from a Mulliken population analysis of the eigenvectors. In Table I the magnetic moments of atoms in clusters of 9, 15, 27, and 51 atoms having bcc geometry and bulk  $V$  lattice spacing are presented. The atoms in the 9-atom cluster possess rather large moments coupled antiferromagnetically between the central and outer-shell atoms. The moment on the central atom is reduced substantially from the free-atom value which, in the local spin density approximation,<sup>1</sup> is  $5\mu_B$ . These moments abruptly vanish when the 9-atom cluster is dressed by a second shell of atoms as the 15-atom cluster. This is very different from other transition elements Fe, Co, and Ni which require larger cluster sizes for the moment on the central atom to converge to bulk value and where the surface atoms show consistently higher moments.

Our prediction that a cluster of  $V$  atoms consisting as few as 15 atoms in the bcc configuration is at odds with the experimental result of Akoh and Tasaki<sup>4</sup> discussed earlier. These authors found  $V$  clusters in the size range of 100–1000 Å to be magnetic. One would expect that  $V$  clusters of this size would very nearly resemble the crystalline structure and its interatomic distance would be al-

TABLE I. Magnetic moments ( $\mu_B$ ) of various sites in  $V$  clusters.

Cluster size	Moment of the atoms in the central and surrounding shells				
	Central	1st	2nd	3rd	4th
9	−1.38	3.42			
15	−0.02	0.02	−0.03		
27	0.00	−0.01	0.01	0.05	
51	0.00	0.00	0.00	0.00	0.004

most identical to the bulk value. Thus, if our theory is correct, these  $V$  particles should not exhibit any magnetic behavior. Since our method has successfully accounted for the magnetic moments of Fe and Ni, it will be worthwhile to repeat the experiment of Akoh and Tasaki with state-of-the-art techniques.

To study the stability of these clusters with respect to magnetic ordering, we have calculated the binding energies of 9- and 15-atom clusters of paramagnetic and antiferromagnetic configurations. The interatomic distances in these clusters were again chosen to conform to the bulk value. We found that for the 9-atom cluster the binding energy is 3.5 eV/atom in antiferromagnetic (AFM) state and 3.1 eV/atom in paramagnetic (PM) state so that the AFM state is 0.4 eV/atom more stable than the PM state. For the 15-atom cluster, both AFM and PM state have the same binding energy of 4.9 eV/atom. These results reaffirm that  $V_9$  cluster is magnetic, but  $V_{15}$  is not, assuming that both have the same lattice constant and bcc configuration as in the bulk.

In order to understand the effect of interatomic distance on the magnetic moments, we have calculated the magnetic moment on the central atom of the  $V_9$  cluster by varying the nearest-neighbor distance,  $R_0$ . In Fig. 2 we plot these moments as a function of  $R/R_0$  where  $R$  is the varying value of the interatomic distance. Note that the moments gradually approach to an asymptotic limit. This limit should in principle be  $5.0\mu_B$  as discussed by Moruzzi *et al.*<sup>6</sup> in the LSD approximation. However, our computed moments at  $R/R_0=1.8$  is  $4.0\mu_B$  which is somewhat smaller than the value obtained by Moruzzi *et al.*, namely,  $4.5\mu_B$  at the same distance of separation. Part of the discrepancy, we believe, could arise due to our choice of basis functions. These were determined to better represent bonding at equilibrium lattice constant distances and may not be appropriate when the distances are too large.

As the interatomic distances are reduced, the moments begin to decrease and abruptly goes to zero at  $R/R_0=0.9$ . Moruzzi *et al.*<sup>6</sup> in their band calculation of  $V$  also observed a similar change in the magnetic moment as the lattice constant were decreased. The moment went

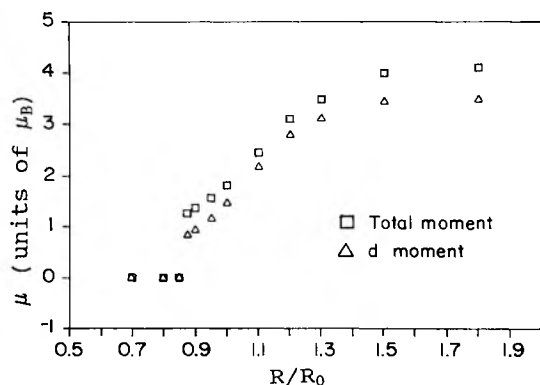


FIG. 2. Magnetic moment at the central site of a 9-atom bcc vanadium cluster as a function of interparticle spacing.

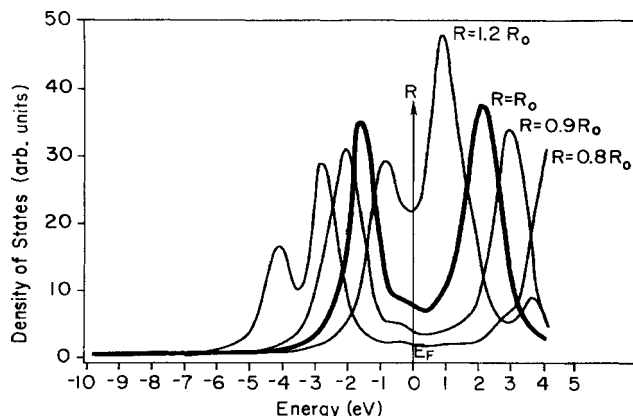


FIG. 3.  $d$  component of the local density of states at the central site of a 9-atom bcc vanadium cluster as a function of interparticle spacing.

to zero at  $R/R_0=1.15$ . The difference between the  $R/R_0$  values where the moments vanish in the cluster and the crystal is clearly a consequence of the size: a cluster being able to retain its moments more effectively than the corresponding crystal.

The loss of magnetism as the interatomic distance decreases can be understood from the simple Stoner criterion<sup>10</sup> which states that for a system to exhibit magnetism, the density of states at the Fermi energy needs to be high ( $Un_{E_F} > 1$ , where  $U$  is the coulomb repulsion). To show this we plot in Fig. 3 the partial density of states for the  $d$  orbital on the central atom of  $V_9$  clusters for various values of  $R/R_0$ . Note that the DOS at the Fermi energy decreases rapidly as  $R/R_0$  is decreased, practically vanishing for  $R/R_0 \sim 0.8$ . As the atoms are pushed towards each other, the overlap between the electron orbitals centered at different atoms increases causing the band to broaden. In addition, the crystal field splits the band into two peaks and this splitting increases as the interatomic spacing is reduced. Since  $V$  has an approximately half-filled  $d$  band, the Fermi energy lies in the middle of the valley. These features conspire to cause a compressed  $V_9$  cluster to become nonmagnetic.

The above findings are also confirmed from energetics calculations. In Fig. 4 we plot the binding energy per atom for the  $V_9$  cluster as a function of  $R/R_0$  for the ferromagnetic, antiferromagnetic, and paramagnetic configurations. For large interatomic separation, the ferro- and antiferromagnetic states have the same energy and are lower than the paramagnetic state. As the interatomic distance decreases, the AFM state becomes more stable and remains the most stable state until  $R/R_0 \sim 0.9$ . At this point the paramagnetic state becomes the most stable state. We want to remind the reader that the ground state of the  $V_9$  cluster held at the equilibrium lattice constant distance is antiferromagnetic. This clearly stresses the importance of the interatomic spacing and, as we will see in the following, the importance of cluster geometry on the magnetic properties. Our calculations on  $V$  clusters should not be taken to im-

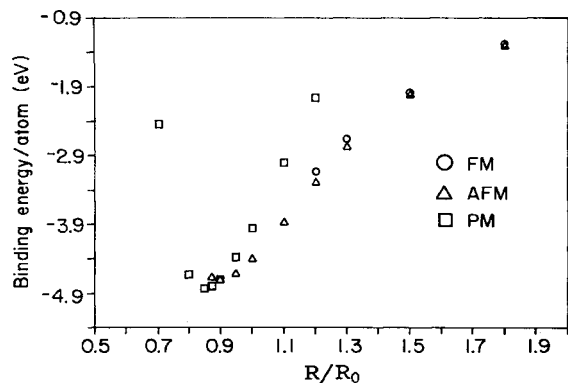


FIG. 4. Binding energy/atom of a 9-atom bcc vanadium cluster for the ferromagnetic (FM), antiferromagnetic (AFM), and the paramagnetic (PM) states as a function of the interparticle spacing.

ply that a cluster of 9 or 15 atoms held in free space would actually form the rudiments of a bcc structure. As a matter of fact, chances are that small clusters of  $V$  in gas phase would have geometries that are very unlike their bulk structures and that the magnetic properties of small gas phase  $V$  clusters could be very different from that studied here. Ideally, what is needed will be a complete geometry optimization of  $V$  clusters and studies of their corresponding magnetic properties. Although such studies are available for simple metals like the alkalis up to 10 atom clusters,<sup>15</sup> these are very difficult for transition metal systems. We are vigorously pursuing the geometries of transition metal clusters and hope that it will be soon possible for us to study the magnetism corresponding to the optimized geometries of transition metal clusters.

To illustrate that a geometry indeed can be important we have turned our attention to a model system where  $V$  atoms are allowed to form linear chains. It seems likely that using the molecular beam epitaxy method, linear chains of atoms could be formed at the steps of a cleaved surface. In Fig. 5 we plot the moments as a function of number of atoms held at the bulk interparticle distance. We note that in the linear chain the moments prefer to

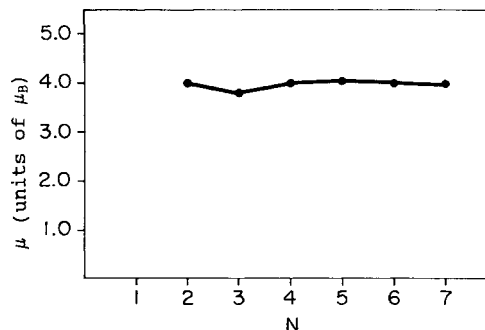


FIG. 5. Magnetic moment per atom of  $V$  chains as a function of the number of atoms,  $N$ , in the chain.

order ferromagnetically. The moments oscillate slightly due to  $s$ - $d$  mixing and converge to the limiting value rather quickly. This result is consistent with earlier findings that lower dimension<sup>16,17</sup> favors magnetic ordering.

The moments of the  $V$  dimer held at the bulk nearest-neighbor distance of  $4.9 a_0$  can be compared with that of the  $V$  dimer in the gas phase where the equilibrium bond length is  $3.3 a_0$ . The moment per atom in the former (later) is  $4.0\mu_B$  ( $1.0\mu_B$ ). This strong dependence of the moment on the interatomic distance in the linear chains is similar to that shown in Fig. 2 again reaffirming that increasing interatomic distance leads to enhanced magnetic moment.

In summary, we have shown through self-consistent calculations that vanadium could exhibit magnetic behavior if its size and dimensionality are reduced and its interatomic spacing is increased. While  $V$  clusters with three-dimensional geometries lose their moments precipitously in very small sizes, they are able to retain their magnetic order when confined to linear chains without any size limitation. These characteristics are easily understandable through the Stoner model and reveal the importance of size and dimensionality on the magnetic behavior.

This work was supported in part by Grant No. DAAL03-89-K-0015 from the Army Research Office.

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